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Possible Pathways for Oxidative Degradation of β-hydroxyl Alkanolamine for Post-combustion CO_2 Capture

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Abstract

Solvent degradation due to the presence of oxygen is an important issue for amine-based absorption/stripping process for post-combustion carbon dioxide capture from flue gas streams. There are still some knowledge gaps in the understanding of alkanolamine oxidation so far. To explore possible degradation mechanism of alkanolamines, oxidative degradation of aqueous β-hydroxyl alkanolamine solutions without CO_2 loading was investigated in the presence of 250 kPa O_2 at 120 °C. The alkanolamines include monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-propanol (APN), and 2-amino-1-butanol (ABN). The anionic oxidation products were identified by anion chromatography. A possible degradation pathway for the oxidative degradation of the investigated amines is proposed to account for the formation of the carboxylic acid products.

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Keywords: CO_2 capture; oxidative degradation; degradation pathway; solvent development

1. Introduction

An amine-based absorption/stripping process is the state-of-the-art technology for post-combustion capture of carbon dioxide (CO_2) from flue gases of fossil fuel-fired power plants. The CO_2 capture is energy intensive, represents about 75~80% of the total cost of CO_2 capture and storage (CCS), and as such largely determines the

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cost of the CCS process [1]. Under varying conditions, amine solvents in post-combustion CO_2 capture (PCC) processes are subject to degradation including thermal degradation, CO_2 induced degradation and oxidative degradation [2]. Solvent degradation has been estimated to be around 10% of the overall CO_2 capture cost using aqueous monoethanolamine (MEA) absorption technology [3]. The presence of oxygen (O_2) in the flue gas streams increases the likelihood of corrosion of equipment. In addition, alkanolamines like MEA can easily be degraded in the presence of O_2 [4]. It is reported that oxidative degradation reactions account for about half the total amine degradation [5, 6]. Hence, degradation of amine-based solvent due to presence of O_2 in the flue gas streams is one of the challenges for its industrial application for PCC.

Technology suppliers are indeed more and more eager to develop new solvents to replace MEA. Information based solely on solvent performance is, however, insufficient for evaluating practicability of the solvent. Other aspects such as degradation and corrosion need to be considered as well. Screening and characterization of solvent oxidative degradation potential has emerged as a critical step in the early stages of solvent selection. Although oxidative degradation of amines relevant to CO_2 capture has been studied for a while, most of the investigations were focused on MEA [7-9]. Even for MEA, there are still some knowledge gaps in the understanding of amine oxidation [10].

In order to explore possible alkanolamine degradation mechanisms, a series of lean (no CO_2 loading) β-hydroxyl alkanolamines, including MEA and 2-amino-2-methyl-1-propanol (AMP), were tested for oxidative degradation in the present work. A possible degradation pathway for β-hydroxyl alkanolamines is proposed mainly based on the observed anionic degradation products.

2. Experimental Methods

All the chemicals (97-99.5%) used in this work were purchased from Sigma-Aldrich or Acros Organics and used as received. The gases (>99.99%) were provided by AGA (Oslo, Norway). The degradation experiments were performed in a 200mL glass autoclave with a stainless steel lock. The amine aqueous solutions were degraded in the presence of 250 kPa oxygen at 120 °C for about two weeks while periodic samples were taken. Details of the reaction system, a typical experimental run and product analysis have been given in our earlier work [11].

The remaining amine in partially degraded samples was determined by cation-exchange chromatography (column: IonPac SCG1with SCS1) with non-suppressed conductivity detection using methane-sulfonic acid as the eluent. Anionic degradation products were identified anion-exchange chromatography (column: IonPac AG15 with AS15) using potassium hydroxide as the eluent. Some non-ionic degradation products were identified by gas chromatography coupled with mass spectrometry (GC-MS; column: DB-5MS).

3. Results and Discussion

3.1. Oxidative degradation of AMP

Aqueous AMP solution with an initial concentration of 5 mol/kg was degraded under 250 kPa O_2 at 120 °C. As shown in Figure 1, the major carboxylic acid product was formate. Small amounts of oxalate, acetate and glycolate were also determined in the degraded AMP samples. Acetone, ammonia (in the cation form, NH_4^+) and formate were identified as major products by GC-MS and ion chromatography. We have proposed a pathway for oxidative degradation of AMP based on the identified products, as illustrated in Figure 2 [11]. Oxidative degradation of AMP is believed to proceed via a radical mechanism. Oxygen participating in the oxidation process is thought to be through formation of a peroxyl radical, which decomposed into primary products through a six-membered transition state by intramolecular hydrogen abstraction and loss of a ·OH radical. According to this proposed degradation pathway, formic acid, acetone and ammonia are the primary degradation products. In the presence of $\cdot OH/O_2$, acetone can be decomposed to form acetic-, oxalic- and glycolic acid [12, 13]. Since formic acid is a primary degradation product, its final concentration is much higher than that of the secondary carboxylate ions. The reactions of AMP and the primary products lead to formation of amides, formation of lutidine, oxazolidinone, and other secondary degradation products [14].

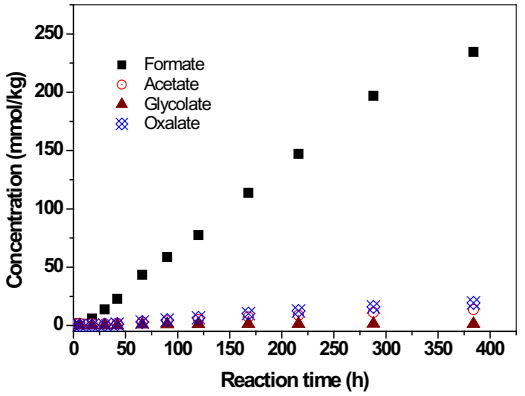

Fig. 1. Formation of carboxylic acids in the AMP degradation experiment (initial concentration of AMP = 5 mol/kg, 120 °C, 250 kPa O_2) [11].

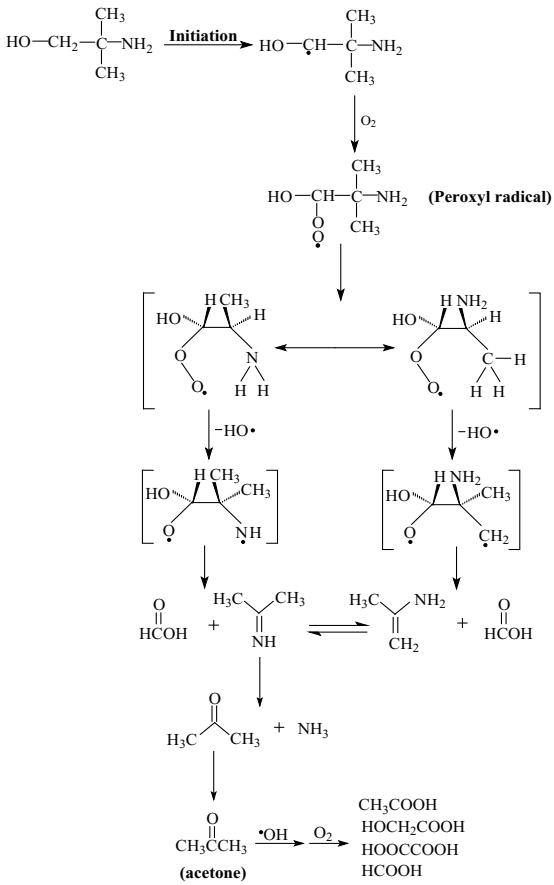

Fig. 2. Scheme for AMP oxidation (adapted from [11]).

3.2. Oxidative degradation of MEA

Aqueous solution of 5mol/kg MEA was also degraded under 250 kPa O_2 at 120 °C. As expected, MEA degraded faster than the other three investigated β-hydroxyl amines. The degradation products were identified by ion chromatography and GC-MS. Figure 3 shows the formation of carboxylates in the degraded MEA samples. Among the quantified carboxylate anions, formate is the most abundant product. After 16 days, concentration of formate in the degraded MEA solution was approximate 46, 27, and 13 times higher than that of acetate, glycolate and oxalate, respectively.

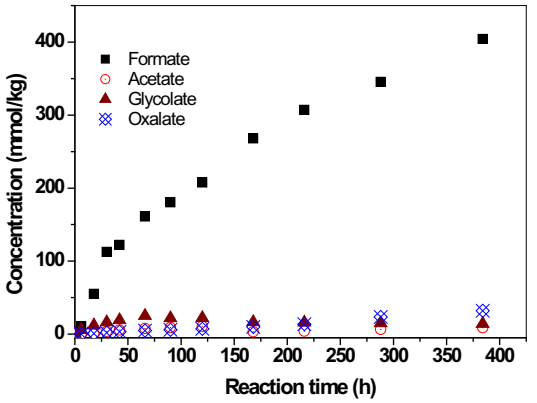

Fig. 3. Formation of carboxylic acids in the MEA degradation experiment (initial concentration of MEA = 5 mol/kg, 120 °C, 250 kPa O_2).

Carboxylic acid formation during oxidative degradation of MEA has been reported by many researchers. Two general mechanisms were proposed for the generation of carboxylic acids by Rooney et al. [15] and Lepaumier et al. [16], which were summarized in a recent review [9]. However, the mechanism of methylamine formation described by Rooney et al. has not been confirmed. The mechanism proposed by Lepaumier et al. does not explain formation of acetic acid [9]. We believe that MEA might be oxidized in a similar pathway as described for AMP in Figure 2.

If MEA is degraded by a similar pathway as proposed for the oxidation of AMP, formic acid could be the unique carboxylic acid product. The pathway for initial hydrogen abstraction and ultimate formation of formic acid is presented in Figure 4 pathway (I). The initial hydrogen abstraction occurs at the C-H bond adjacent to the OH group. After initiation, the degradation pathway could be speculated to be similar as what described for AMP degradation in Figure 2. Forming of a carbon-centered radical is followed by the production of a peroxyl radical in the presence of dissolved O_2 in aqueous solution. The peroxyl radical could decay by intramolecular hydrogen abstraction from the $–NH_2$ group through a six-membered cyclic transition state. After ejection of a ·OH from this transition state, it could decompose to formic acid and an imine. The imine is not stable in aqueous solution, and would hydrolyze to ammonia and formaldehyde. Formaldehyde is easily oxidized to formic acid. Thus formic acid would be the primary anionic products.

However, since the MEA molecule has two α-hydrogen atoms, the initiation step could also take place via abstraction of a hydrogen atom at α-C-H bond, as shown in Figure 4 pathway (II). This pathway explains formation of acetic-, glycolic-, and oxalic acid.

It should be noted that N-(2-hydroxyethyl) oxamate (HEO) has been detected as an anionic product in significant amounts. This product can be explained simply by reaction of MEA with oxalic acid, as MEA reacts with formic- and acetic acid to form N-(2-hydroxyethy)formaide (HEF) and (2-hydroxyethyl)acetamide (HEA), which have been identified in the degraded MEA solution by GC-MS. Formation of HEF, HEA, and HEO in the case of MEA suggests that carboxylic acids play one more role in further degradation of the solvent in addition to the well known heat stable salt forming reaction.

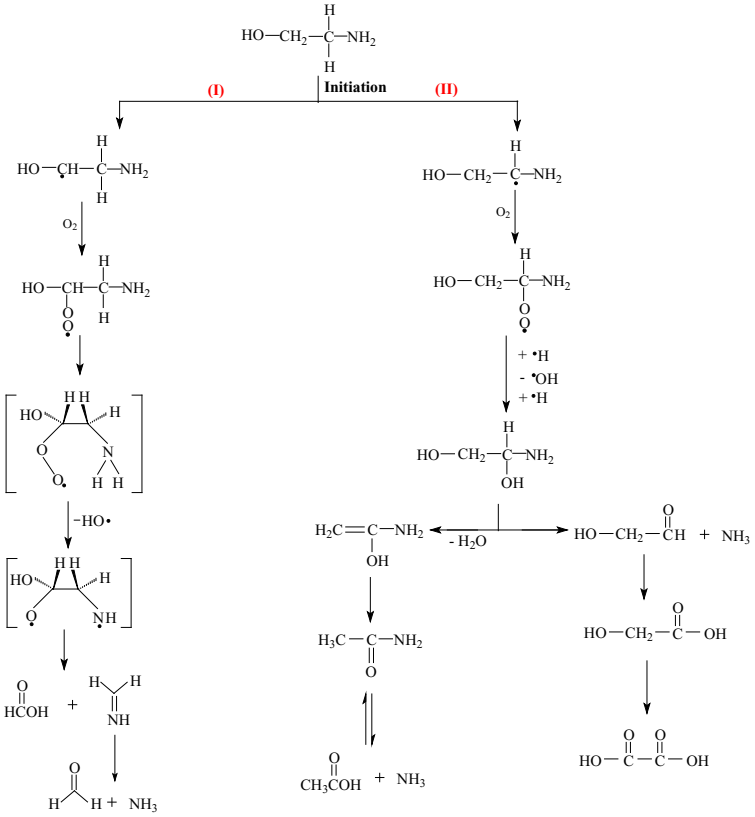

Fig. 4. Scheme for MEA oxidation.

3.3. Oxidative degradation of APN and ABN

As compared to AMP, one of the two methyl group on the α-carbon is replaced by a hydrogen atom in 2-amino-1-propanol (APN) molecule. This means that APN is only slightly sterical hindered and the effect of the single additional methyl group should be 'milder' than two additional methyl group in AMP. As expected, the overall degradation rate of APN is faster than AMP but slower than MEA.

If APN is degraded by a similar pathway as proposed for the oxidation of AMP and MEA, acetic-, formic-, and pyruvic acid could be the major carboxylic acid products. The pathway for initial hydrogen abstraction and ultimate formation of the carboxylic acids is presented in Figure 5. Pyruvic acid is reported to be instable in the presence of ·OH radicals [13]. It can ultimately decay to oxalic- and formic acid.

The partially degraded APN samples were analyzed by anion IC. All the expected carboxylate products were identified and quantified in the partially degraded aqueous APN solution with an initial concentration of 3 mol/kg. (see Figure 6). As can be seen, acetate is the predominant carboxylate product. As proposed in Figure 5, acetic acid is a primary product and acetate can hence accumulate in much higher concentration in APN solution as compared to AMP and MEA. According to the proposed pathway in Figure 5, the molar ratio of acetate to formate should be smaller than 1:1. However, the experimental result shows that the ratio was higher than 1 and increased with reaction time. This is probably due to mineralization of the carboxylic acids, since formic acid is oxidizable at a much higher rate constant by ·OH radicals than acetic acid [17]. During the oxidation of APN, ·OH radical concentration is not sufficient for complete mineralization of the carboxylic acids, and hence more formic acid is consumed than acetic acid, which leads to a higher end of concentration of acetic acid as compared to formic acid. It is also because of insufficient ·OH radical that pyruvic acid can be detected in the partially degraded APN samples.

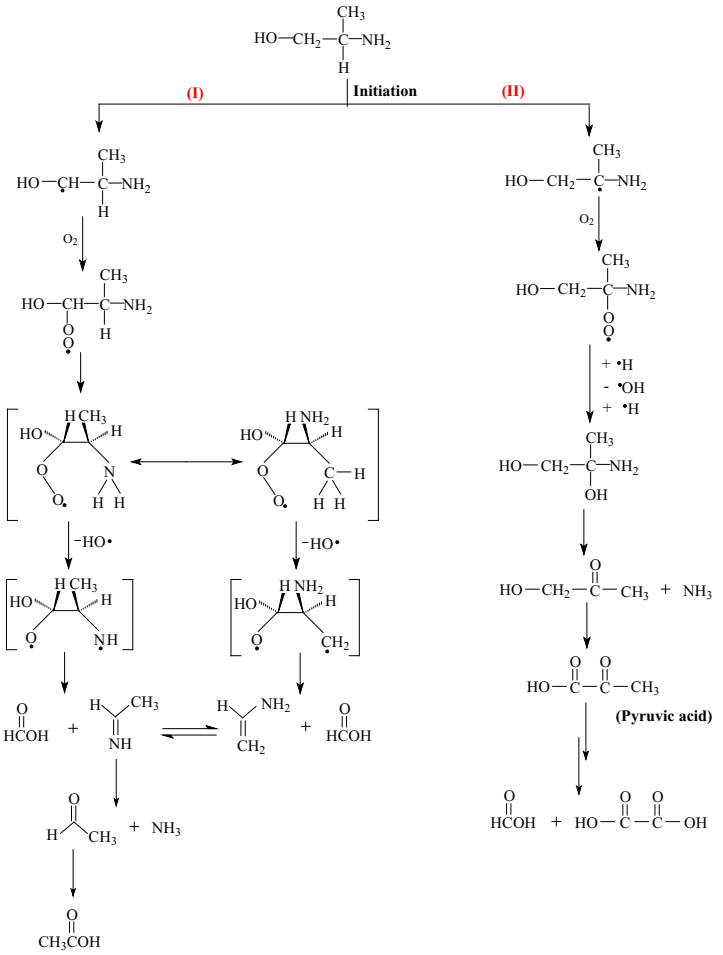

Fig. 5. Scheme for APN oxidation.

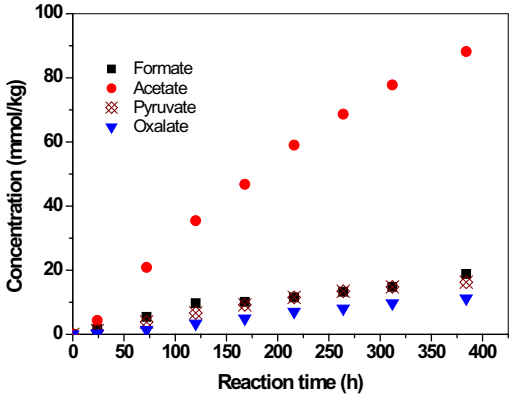

Fig. 6. Formation of carboxylic acids in the APN degradation experiment (initial concentration of APN = 3 mol/kg, 120 °C, 250 kPa O_2).

2-amino-1-butanol (ABN) molecular structure is similar as APN, just the α-methyl group in APN molecule is replaced by an ethyl group in ABN molecule. An aqueous solution with an initial concentration of 3 mol/kg ABN was degraded in this work. The anionic analysis result (see Figure 7) shows that propionate is the predominant carboxylate product. It is likely that ABN can also be degraded as the pathway proposed for the previous alkanolamines. Propionate formation during ABN degradation might follow a similar pathway as proposed for APN oxidation as shown in Figure 5 Scheme (I).

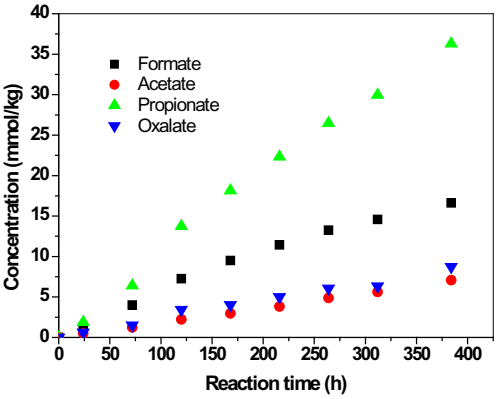

Fig. 7. Formation of carboxylic acids in the ABN degradation experiment (initial concentration of ABN = 3 mol/kg, 120 °C, 250 kPa O_2).

4. Conclusions

Oxidative degradation of four β-hydroxyl alkanolamines was investigated at 120 °C and 250 kPa O_2. Mainly based on the identified carboxylic acid products of the investigated β-hydroxyl alkanolamines and the context of the current amine degradation, a possible degradation pathway is proposed for the formation of the identified carboxylic acids. The likelihood of a hydrogen-abstraction step initiates the oxidative degradation of the alkanolamines. Once a C-centered radical is formed, it can be converted to a peroxyl radical quickly by coupling with oxygen. Decomposition of the formed peroxyl radical by intramolecular and intermolecular hydrogen-abstraction leads to the primary product formation. This is probably the one of the main oxygen containing pathways towards the primary alkanolamine oxidation.

Acknowledgements

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References

[1] Davison J. Performance and costs of power plants with capture and storage of CO_2. Energy 2007; 32: 1163–1176.
[2] Bedell S.A. Amine autoxidation in flue gas CO_2 capture-Mechanistic lessons learned from other gas treating processes. Int. J. Greenh. Gas Con. 2011; 5: 1-6.
[3] Rao A.B. and Rubin E.S. A technical, economic, and environmental assessment of amine-based CO_2 capture technology for power plant greenhouse gas control. Environ. Sci. Technol. 2002; 36: 4467-4475.
[4] Davidson, R.M. Post-combustion Carbon Capture from Coal Fired Plants – Solvent Scrubbing. IEA Clean Coal Centre, CCC/125; 2007.
[5] Strazisar B.R., Anderson R., White C.M. Degradation pathways for monoethanolamine in a CO_2 capture facility. Energy & Fuels 2003; 17: 1034-1039.
[6] Sexton A.J. and Rochelle G.T. Reaction products from the oxidative degradation of monoethanolamine. Ind. Eng. Chem. Res. 2011; 50: 667-673.
[7] Chi S. and Rochelle G. T. Oxidative degradation of monoethanolamine. Ind. Eng. Chem. Res., 2002, 41: 4178-4186.
[8] Goff G.S., Rochelle G.T. Monoethanolamine degradation: O_2 mass transfer effects under CO_2 capture conditions. Ind. Eng. Chem. Res. 2004; 43: 6400-6408.

[9] Gouedarda C., Picq D., Launayc F., Carrette P-L. Amine degradation in CO_2 capture. I. A review. Int. J. Greenh. Gas Cont. 2012; 10: 244-270.
[10] Da Silva E.F., Lepaumier H., Grimstvedt A., Vevelstad S.J., Einbu A., Vernstad K., Svendsen H.F., Zahlsen K. Understanding 2-ethanolamine degradation in postcombustion CO_2 capture. Ind. Eng. Chem. Res. 2012; 51: 13329-13338.
[11] Wang T. and Jens K-J. Oxidative degradation of aqueous 2-amino-2-methyl-1-propanol solvent for post-combustion CO_2 capture. Ind. Eng. Chem. Res. 2012; 51: 6529-6536.
[12] Stephan M.I., Hoy A.R., Bolton J.R. Kinetic and mechanism of degradation and mineralization of acetone in diluted aqueous solution sensitized by UV photolysis of hydrogen peroxide. Environ. Sci. Technol. 1996; 30:2382-2390.
[13] Stephan M.I., Bolton J.R. Reinvestigation of the acetone degradation mechanism in diluted aqueous solution by the UV/H_2O_2 process. Environ. Sci. Technol. 1999; 33: 870-873.
[14] Wang T. Degradation of f aqueous 2-amino-2-methyl-1-propanol solvent for carbon dioxide capture. Telemark University College. PhD Dissertation; 2013.
[15] Rooney P.C., Dupart M.S., Bacon T.R. Oxygen's role in alkanolamine degradation. Hydrocarbon Processing 1998, 77: 109–113.
[16] Lepaumier, H., 2008. Étude des mécanismes de dégradation des amines utilises pour le captage du CO_2 dans les fumées. Université de Savoie. PhD Dissertation; 2008.
[17] Chin M. and Wine P.H. A temperature-dependent competitive kinetics study of the aqueous-phase reactions of OH radicals with formate, formic acid, acetate, acetic acid, and hydrated formaldehyde. In: Helz G.R., Zepp R.G., Crosby D.G. (Eds.), Aquatic and Surface Photochemistry. Lewis Publishers, 85-96: 1994.